

Thermodynamic Study of Binary Liquid Mixtures of Xylene and 1,2-dichloroethane at T = 303.15 K

HARISH KUMAR¹, DHEERAJ KUMAR¹ and SUMAN YADAV²

¹Department of Chemistry, Ch. Devi Lal University,
Sirsa, Haryana– 125 055 INDIA.

²Department of Chemistry, Swami Shraddhanand College,
University of Delhi, Alipur, INDIA.

(Received on : June 1, 2012)

ABSTRACT

Thermodynamic studies like density (ρ), specific gravity, ultrasonic speed (u) and excess molar volume (V_m^E) and excess molar enthalpy of binary liquid mixtures of p-xylene + 1,2-dichloroethane have been carried out over the different range of composition at 303.15 K. Thermodynamic parameters like isentropic compressibility K_s , intermolecular free length, L_f , Relative association, R_a , have been computed from experimental findings. The excess thermodynamic functions have been fitted to the Redlich-Kister polynomial equation. The experimental ultrasonic speeds have been analyzed in terms of Jacobson Free Length Theory (FLT), Schaaff's Collision Factor Theory (CFT), Nomoto's relation, and Van Dael's ideal mixture relation. Intermolecular Free Length, L_f , and available volume, V_a , have been calculated from FLT, CFT and thermoacoustic approach. It is observed that density, specific gravity and relative association increases and ultrasonic speed, isentropic compressibility and intermolecular free length decreases with the mole fraction of 1,2-dichloroethane. It is found that intermolecular interactions present between binary liquid mixtures are stronger than pure solvent-solvent interactions. Observed negative values of excess molar volume and first negative and then positive value of molar excess enthalpy confirms the presence of specific chemical attractive force of interactions between the two binary liquid mixtures.

Keywords: Ultrasonic speed, Excess molar volume, p-xylene and 1,2-dichloroethane.

INTRODUCTION

The measurement of thermodynamic and acoustic properties contributes to the understanding of the physicochemical behavior of the binary and multi-component liquid mixtures. Excess properties of liquid systems, such as molar volumes, are required for testing the theories of solutions, development of separation techniques and equipment, and for other industrial applications. *p*-Xylene is used on a large scale for the manufacture of terephthalic acid for polyester. Its polymer is known as Parylene. *p*-Xylene is produced by catalytic reforming of petroleum naphtha as part of the BTX aromatics (benzene, toluene and the xylene isomers) extracted from the catalytic reformat. Its melting point is the highest among this series of isomers. It is also highly flammable. The chemical compound 1,2-dichloroethane, commonly known by its old name of ethylene dichloride (EDC), is a chlorinated hydrocarbon, mainly used to produce vinyl chloride monomer (chloroethene), the major precursor for PVC production. It is a colourless liquid with a chloroform-like odour. 1,2-Dichloroethane is also used generally as an intermediate for other organic chemical compounds and as a solvent. Thus, a study of physical properties data on the binary mixture containing 1,2-dichloroethane and *p*-xylene has attracted considerable interest in the literature¹⁻³. Thus, 1,2-dichloroethane in *p*-xylene mixed solvent would enable us to have a large number of solvents with appropriate physico-chemical properties, which can be

used for a particular chemical process. Moreover, literature survey indicates that no transport and thermodynamic study on this binary system has been reported at 303.15 K. Therefore, present study was undertaken in order to have deeper understanding of the intermolecular interaction between the components of the above binary liquid mixture. Thus, a study of thermodynamic properties data on the binary mixture of 1,2-dichloroethane in *p*-xylene has attracted considerable interest in our present study.

Research workers in the past have shown that NMR^{4,5}, IR⁶⁻⁷ and Raman spectra⁸, have been used to study molecular interactions. The velocity measurement of the propagation of ultrasonic waves⁹⁻¹³ and their absorption^{14,15} have already been found to be useful in the study of molecular interactions for inorganic, organic and organo-metallic binary systems. Likewise, researchers¹⁶⁻²¹ have also employed ultrasonic measurements to look into the important consequences of ion-solvent interactions for the structure of electrolytic solutions. References^{22,23} related to the field of medicine, whereas references²⁴⁻²⁷ based on studies on emulsions/microemulsions, polymer surfactants interactions²⁸ and ultrasonic destruction of surfactants²⁹ are only a few cases to suggest versatility of the technique.

EXPERIMENTAL

1,2- dichloroethane (CAS No. 107-06-2) was procured from Fischer Scientific Ltd. and are further purified by the methods given in Vogel text book of practical organic

chemistry³⁰. Prior to the experimental measurements, all the organic liquids were stored in dark bottles over 0.4 nm molecular sieves to reduce water content and were partially degassed with a vacuum pump under nitrogen atmosphere. The purities of all the samples determined by chromatographic analysis were better than 0.996 on a molar basis. Binary mixtures are prepared by mixing appropriate volumes of the liquid component in the specially designed glass bottles with air tight Teflon coated caps. The required properties are measured on the same day immediately after preparing each composition. The uncertainty in mole fraction is ± 0.0001 . A multi frequency digital micrometer reading ultrasonic interferometer (M-81, Mittal Enterprises, New Delhi) operating at 1, 2, 3 and 4 MHz was used to measure the ultrasonic velocity of the binary liquid mixtures (with an uncertainty of $\pm 0.3\%$) at a constant temperature of 303.15 K by using a digital constant temperature water bath. The temperature stability is maintained within ± 0.001 K by circulating thermostated water around the cell with a circulating pump connected to water bath. In order to minimize the uncertainty of the measurement, several maxima are allowed to pass and their number (fifty) is counted. All maxima are recorded with the highest swing of the needle on the micrometer scale. The total distance, d (cm) moved by the reflector is given by $d = \frac{n\lambda}{2}$, where λ is the wavelength. The frequency ν , of the crystal being accurately known (2.0 MHz), the speed of sound, u in ms^{-1} is calculated by using the relation $u = \lambda\nu$. Molar excess

volume, V_m^E was calculated by specially designed double limbed glass dilatometer fitted with a microcapillary (± 0.01 cm) in the centre. The density of solution was measured by a double arm pycnometer of bulb capacity 10 ml and a capillary of an internal diameter of about 1.0 mm. The mark of the stem was calibrated by double distilled water (conductivity less than 1×10^{-6} $\text{ohm}^{-1} \text{cm}^{-1}$) with 0.9970 and 0.9940 g cm^{-3} as its density at 298.15 K and 303.15 K, respectively with buoyancy corrected. The accuracy of the density results was ± 0.0001 (g cm^{-3}). Before each series of measurements, the instrument was calibrated with triple distilled freshly degassed water. The density and ultrasonic speed of binary mixtures were also measured by an Anton Paar Densitometer (DSA 5000). The accuracy of the density results was ± 0.00001 (g/cm^3). Molar excess enthalpy was measured using two drop calorimeter Model 4000, Calorimetric Scientific Corporation, CSC. Weight measurement were performed on a Mettler Toledo AB 135-S/FACT, single pan analytical balance, with a precision of 0.01 mg. The densities, and ultrasonic speed, u of the pure liquids were in good agreement with the values found in the literature and are presented in Table 1.

RESULTS

The molar excess volumes, V_m^E , of the solution were calculated from the densities of the pure liquids and their mixtures using the following equation³¹

$$V_m^E = \frac{(x_1 M_1 + x_2 M_2)}{\rho_{\text{mix}}} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (1)$$

Where ρ_{mix} is the density of the mixture and x_1, M_1, ρ_1 and x_2, M_2, ρ_2 are the mole fraction, molar mass, and the density of pure component 1 and 2, respectively.

The following relations have been used to correlate the sound velocity, u , of the binary liquid mixtures:

Nomoto Relation³²

$$u = \left(\frac{R_m}{V_{mix}} \right)^3 = \left(\frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right)^3 \quad (2)$$

Where x_1, x_2, V_1, V_2 and R_1, R_2 are mole fractions, molar volumes, and molar sound velocity of first and second components, respectively.

Van Dael Relation³³

$$\frac{1}{x_1 M_1 + x_2 M_2} \cdot \frac{1}{u_{id,mix}^2} = \frac{x_1}{M_1 u_1^2} + \frac{x_2}{M_2 u_2^2} \quad (3)$$

Where, M_1, M_2 and u_1, u_2 are the molar masses and sound velocities of first and second components, respectively, and $u_{id,mix}$ is the ultrasonic velocity of the ideal mixture.

Jacobson's Free Length Theory (FLT)³⁴

$$u_{mix} = \frac{K}{L_{f(mix.)} \rho_{mix}^{1/2}} \quad (4)$$

Where K is the Jacobson constant which is temperature dependent only and its value is 642.15 at 313.15 K. The $L_{f(mix.)}$ is the

intermolecular free length of the binary mixtures, which is given by $L_f = \frac{2V_a}{Y}$.

Here V_a represents the available volume per mole and Y is the surface area per mole and these may be expressed as

$$V_a = (V_T - V_0) \quad (5)$$

$$Y = (36\pi N_A V_0^2)^{1/3} \quad (6)$$

Here N_A is the Avogadro's number and V_0 and V_T are the molar volumes at zero Kelvin and at temperature T , respectively. The V_0 can be obtained from the following relation using critical temperature T_C :

$$V_0 = V_T \left(1 - \frac{T}{T_c} \right)^{0.3} \quad (7)$$

The critical temperature, T_C is the mole fraction additive of the values of its pure components and is given by the relation:

$$T_C = x_1 T_{C(1)} + x_2 T_{C(2)} \quad (8)$$

The thermodynamic intermolecular free lengths, L_f , in the binary liquid mixtures have been calculated using the relation:

$$L_f = 2 \frac{[V_T - \{x_1 V_{0(1)} + x_2 V_{0(2)}\}]}{(x_1 V_1 + x_2 V_2)} \quad (9)$$

The ultrasonic intermolecular free lengths L_f , have also been computed using the Schaaff's relation for available volume (V_a):

$$V_a = V_T \left[1 - \frac{u}{u_\infty} \right] \quad (10)$$

Where, u is the ultrasonic velocity at temperature T and u_∞ is 1600 m.s^{-1} .

Schaaff's Collision Factor Theory (CFT)^{35,36}

$$u_{mix} = u_\infty (x_1 s_1 + x_2 s_2) \frac{[x_1 b_1 + x_2 b_2]}{V_{mix}} \quad (11)$$

Where, b and s are the geometric volume and collision factor, respectively. The actual volume of the molecule per mole of the liquid has been computed using the relations

$$b = \frac{4}{3} \pi r^3 N \quad (12)$$

Where, r is the molecular radius which has been computed using the Schaaff's relation³⁶

$$r = \left(\frac{M}{\rho N} \right)^{1/3} \left[\frac{3}{16\pi} \left[1 - \frac{\gamma RT}{Mu^2} \left(\sqrt{1 + \frac{Mu^2}{3\gamma RT}} - 1 \right) \right] \right]^{1/3} \quad (13)$$

$$b' = \left[\frac{M}{\rho} - \frac{\gamma RT}{\rho u^2} \left(\left(1 + \frac{Mu^2}{3\gamma RT} \right)^{1/2} - 1 \right) \right] \quad (14)$$

$$r = \left(\frac{3b'}{16\pi N} \right)^{1/3} \quad (15)$$

Where, b' is the van der Waal's constant and is equal to four times the actual volume of

the molecules per mole of the liquid, i.e. $b' = 4b$.

The thermoacoustical method³⁷⁻³⁹ has also been employed to obtain the available volume, V_a using the relation

$$V_a = V_T \left(\frac{1}{K' + 1} \right) = V_T \left(\frac{1}{K'' + K' + 1} \right) \quad (16)$$

The K' , K , and K'' are known as isothermal, isobaric and isochoric acoustical parameters, respectively, and can be expressed by the relation

$$K' = K + K'' = \frac{1}{2} \left[3 + \frac{S^* (1 + \alpha T) + X}{\alpha T} \right] \quad (17)$$

$$K'' = 1 + \frac{X}{2\alpha T} \quad (18)$$

$$K = \frac{1}{2} \left[1 + \frac{S^* (1 + \alpha T)}{\alpha T} \right] \quad (19)$$

$$S^* = 1 + \frac{4\alpha T}{3} \quad (20)$$

The X is known as the isobaric temperature coefficient of internal pressure and can be expressed as

$$X = 2 \frac{(1 + 2\alpha T)}{\tilde{V}^{C_1}} \quad (21)$$

Where $\tilde{V}$ represents the reduced molar volume and C_1 is the Moelwyn-Hughes parameter and can be expressed as

$$\tilde{V} = \left[\frac{\alpha T / 3}{1 + \alpha T} + 1 \right] \quad (22)$$

$$C_1 = \frac{13}{3} + \frac{1}{\alpha T} \frac{4\alpha T}{3} \quad (23)$$

The thermal expansion coefficient, α , has been calculated using the equation:

$$\alpha = \left(\frac{1}{\rho} \right) \left(\frac{\partial \rho}{\partial T} \right)_p \quad (24)$$

The isentropic compressibility has been calculated from Newton-Laplace's equation

$$k_s = \frac{1}{\rho u^2} \quad (25)$$

The excess isentropic compressibility was found out by using the relation,

$$k_s^E = k_s - k_s^{id} \quad (26)$$

Where, k_s^{id} the isentropic compressibility for the ideal mixture, was obtained according to Benson and Kiyohara⁴⁰ and Acree⁴¹:

$$k_s^{id} = \sum_i \phi_i \left[k_{s,i} + \frac{TV_i \alpha_i^2}{C_{p,i}} \right] - T \left(\sum_i x_i V_i \right) \frac{\left(\sum_i \phi_i \alpha_i \right)^2}{\left(\sum_i x_i C_{p,i} \right)} \quad (27)$$

Where, ϕ_i is the volume fraction of component i in the mixture, x_i is the corresponding mole fraction, T is the

absolute temperature, and $k_{s,i}$, V , α_i and $C_{p,i}$ are the isentropic compressibility, the molar volume, the cubic expansion coefficient, and the molar heat capacity of pure components respectively. The cubic expansion coefficients were obtained from experimental density measurements performed in our laboratory at different temperatures.

The excess isentropic compressibility of the binary mixture were fitted with a Redlich-Kister polynomial equation⁴²

$$k_s^E = x_1 x_2 \sum_{j=0}^n A_j (x_1 - x_2)^j \quad (28)$$

Where, A_j are the adjustable parameters.

Oswal⁴³ extended the Prigogine-Flory-Patterson (PFP) theory to estimate the isentropic compressibility's and speeds of sound of liquid mixtures. At a given temperature, T , the PFP theory can be used to calculate the molar volumes, V and the molar heat capacities, C_p , of a liquid mixture if the interaction parameter, χ_{12} , is known.

Inter molecular free length and relative association has been calculated by the following formula:

$$L_f = K (K_s)^{1/2} \quad (29)$$

$$R_A = \frac{\rho}{\rho_0} \left(\frac{u_0}{u} \right)^{1/3} \quad (30)$$

Where ρ_0 and u_0 are the densities and ultrasonic speed of pure solvent, ρ and u are

the density and ultrasonic speed of mixture respectively and K is the temperature dependent Jacobson constant (6.0816×10^4 at 35°C).

The deviation parameters of binary liquid mixtures have been evaluated using the general equation:

$$\Delta Y = Y_{\max} - (X_1 Y_1 + X_2 Y_2) \quad (31)$$

Where, Y indicates the parameter such as isentropic compressibility, inter molecular free length and ultra sonic speed. X_1 and X_2 are the mole fraction of component 1 and 2 respectively. ΔY , Y_1 , Y_2 , and $Y_{\max}$ are the deviation parameter, parameters of the component 1 and 2 and observed parameters, respectively.

The number of contact sites per segment of a molecule, has been estimated using Bondi's method⁴⁴. Molecular interaction parameter for each binary mixture was obtained by fitting the PFP theory to the corresponding experimental equimolar H^E values^{45,46}. Once the interaction parameter is obtained, the isentropic compressibility and the speed of sound can be estimated.

Physical properties of pure substance like density, ultrasonic speed at 308.15 K are shown in Table 1. Density, speeds of sound, u , and specific gravity of binary liquid mixture of 1,2-dichloroethane in p-xylene over the different composition range at a temperature of 308.15 K are reported in Table 2. Values of molar excess volume, V_m^E , isentropic compressibility, k_s , intermolecular free length, L_f , and relative association, R_a , of the binary liquid mixture

is shown in Table 3. Table 4 shows molar excess volume of the binary liquid mixture of 1,2-dichloroethane in p-xylene at 308.15 K. Theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's (NOM) and Van Dael and Vangeel's (VD) ideal mixing relation were compared with experimental values and their percentage error for 1,2-dichloroethane (1) + p-xylene (2) at 303.15 K were shown in Table 4. The values of the coefficients of Redlich-Kister polynomial equation for all the binary mixtures along with values of the standard deviation are represented in Table 5 for 1,2-dichloroethane in p-xylene binary liquid mixture at 308.15 K.

Table 6 shows Intermolecular Free Length, L_f , calculated from Free Length Theory (FLT), Collision Factor Theory (CFT), and Thermoacoustic Approach (TAP). Table 7 shows available volume, V_a , calculated from FLT, CFT and TAP for 1,2-dichloroethane (1) + p-xylene (2) binary liquid mixture at 308.15 K.

Figure 1 shows variation of molar excess volume with the mole fraction of 1,2-dichloroethane in p-xylene binary liquid mixture. Figure 2 shows variation of molar excess enthalpy with the mole fraction of 1,2-dichloroethane in p-xylene binary liquid mixture.

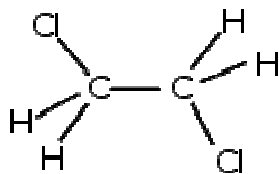
DISCUSSION

Density and specific gravity of binary liquid mixtures of 1,2-dichloroethane in p-xylene increases with the mole fraction of 1,2-dichloroethane while ultrasonic speed decreases with the mole fraction of 1,2-dichloroethane (Table 2). Binary systems of 1,2-dichloroethane in p-xylene shows

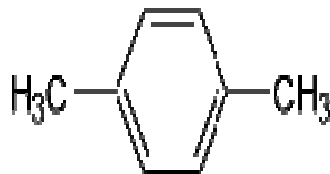
decrease in isentropic compressibility over entire range of mole fraction of 1,2-dichloroethane. From Table 3, it is observed that the values of excess molar volume are negative while values of isentropic compressibility are positive, such trends of negative value of speed of sound and

positive value of isentropic compressibility is quite common⁴⁷⁻⁵².

In pure 1,2-dichloroethane there is the usual dispersive interaction. The effect of adding a non polar second component is primarily to disrupt the dispersive interaction of the first component.



1,2-dichloroethane



para-xylene

The behavior of binary liquid mixtures can be explained in term of 1) physical forces -dispersion 2) chemical forces – dipole-dipole interaction⁵³. The former factor increases the intermolecular free length as described by Jacobson⁵⁴. This in turn, causes negative deviation in sound speed and positive deviation in compressibility. On the other hand, the latter factor decreases the intermolecular path lengths leading to a positive deviation in sound speed and negative deviation in compressibility and excess molar volume, V_m^E . The actual values depend upon the relative strength of two opposing effects. The observed positive values of K_s^E and negative value of excess molar volume (Table 3) imply that there are attractive specific chemical interaction between the two unlike molecules.

Since, V_m^E is a packing effect and H_m^E is an interactional effect between the A and B constituents of an (A+B) mixture and

as V_m^E data of the 1,2-dichloroethane in p-xylene binary liquid mixtures are negative throughout the composition range of p-xylene, this suggests that as compared to the dispersion forces, negative value of V_m^E in general, always cause close packing of the molecules due to specific attractive chemical interaction between the two unlike molecules. Their respective contribution to the measured data is a function of the mole fraction of 1,2-dichloroethane.

The conclusion is further fortified by the increasing value of relative association, R_A included in Table 3. All the trends of the above parameters indicate that the mixtures are less compressible than their corresponding ideal mixtures. Generally, the deviation parameter is considered to be the reflecting agents of the magnitude of polarity at the site of interaction in the molecules⁵⁵.

The intermolecular free length, L_f , can be related to the space filling ability

assuming that the molecules are incompressible hard spheres having uniform radius. The study of standard deviations, $\sigma(k_s^E)$, presented in Table 5, reveals that the results of ultrasonic velocity for 1,2-dichloroethane with p-xylene systems can be satisfactorily explained by Van Deal Ideal Mixture relation (minimum < 0.12).

It is observed that value of density and relative association increases with increase in mole fraction of 1,2-dichloroethane in p-xylene (Table 2 & 3). The value of ultrasonic speed decreases with increase in mole fraction of 1,2-dichloroethane in p-xylene (Table 2). This is the general trend showing presence of strong intermolecular interaction between the two binary liquid mixtures. The decrease in the value of intermolecular free length with increase in mole fraction of 1,2-dichloroethane in p-xylene (Table 3) further confirms presence of attractive intermolecular forces between the two binary liquid mixtures. The value of intermolecular free length decreases with increase in magnitude with the mole fraction of 1,2-dichloroethane in the binary liquid mixtures. Above results were further supported by the values of relative association. It is observed that value of relative association increases with increase in mole fraction of 1,2-dichloroethane in p-xylene (Table 3). It further confirms presence of specific chemical interaction between the two binary liquid mixtures in comparison to pure liquids.

From Table 3, the decrease in the value of intermolecular free length substantiate the above argument undoubtedly and undeniably unveils the fact the specific

interaction are being operative between the molecules of solvent and co-solvents in the mixture. The negative value of molar excess volume increases up to middle i.e. up to mole fraction of 0.6589 and then decreases (Figure 1). The observed negative values of molar excess volume (Table 3) indicates presence of specific chemical interaction between the binary liquid mixtures of 1,2-dichloroethane and p-xylene.

The H^E values of 1,2-dichloroethane + p-xylene are negative up to a mole fraction of 0.6237 and then positive (Figure 2). The excess heat is thus markedly asymmetrical in this system. Such asymmetry is common in mixtures in which specific interactions occur⁵⁶. It is, however, difficult to comment specifically about the nature of these interactions from thermodynamic evidence alone. A weak complex formation⁵⁷ between the n-electrons of p-xylene under the present investigation with 1,2-dichloroethane could be a probable explanation for the results obtained.

Theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's (NOM) and Van Dael and Vangeel's (VD) ideal mixing relation were compared with experimental values and their percentage error for 1,2-dichloroethane (1) + p-xylene (2) at 303.15 K were shown in Table 4. It is observed that value of theoretical ultrasonic speed calculated from free length theory was found to be in close agreement with the experimental values. The value of theoretical ultrasonic speed calculated from Nomotos relation shows large deviation from experimental values.

The intermolecular free length, L_f , can be related to the space filling ability

assuming that the molecules are incompressible hard spheres having uniform radius. The intermolecular free length, L_f , obtained using free length theory (FLT) for the (1,2-dichloroethane + p-xylene) decreases with the increase in mole fraction of 1,2-dichloroethane (Table 6). However, the L_f value obtained from Schaaf's collision factor theory (CFT) increases with the increase in the mole fraction of 1,2-dichloroethane. The change in the slope of the isotherms of L_f as a function of mole fraction in the higher mole fraction region predicted by FLT and CFT shows that the entropy effect related to the structural rearrangement of solvent molecules due to disruption of dispersive interactions between like molecules. However, the thermoacoustic approach (TAP) predicts that the L_f values in these binary mixtures decreases with increase in the mole fraction of 1,2-dichloroethane. The L_f values for these binary mixtures obtained from the ultrasonic

methods are higher than those obtained from the free length theory and the thermoacoustical approach.

The available volume, V_a , obtained using Free Length Theory (FLT) for the (1,2-dichloroethane + p-xylene) decreases with the increase in mole fraction of 1,2-dichloroethane (Table 7). However, the V_a value obtained from Schaaf's Collision Factor Theory (CFT) increases with the increase in the mole fraction of 1,2-dichloroethane. The change in the slope of the isotherms of available volume as a function of mole fraction in the higher mole fraction region predicted by FLT and CFT shows that the entropy effect related to the structural rearrangement of solvent molecules due to stronger specific chemical interactions between unlike molecules of xylene in 1,2-dichloroethane. However, the thermoacoustic approach (TAP) predicts that the V_a values in these binary mixtures decrease with increase in the mole fraction of 1,2-dichloroethane.

Table 1. Comparison of experimental densities, ρ of pure liquids with literature values at 298.15K, ultrasonic speed, u and molar volume, V^0 at 303.15K.

Components	ρ (g cm ⁻³)		u (m s ⁻¹)		V^0 (cm ³ mol ⁻¹) at 308.15K
	Expt.	Lit.	Expt.	Lit.	
p-xylene	0.8643	0.8614	1283	1281	137.4
1,2- dichloroethane	1.2537	1.2542	1272#	1270#	53.2

value at 298.15K

Table 2. Density, ultrasonic speed and specific gravity of the binary liquid mixture of 1,2-dichloroethane (1) + p-xylene (2).

Mole fraction (X_1)	Density (g/cc)	Ultrasonic speed (u) (m/s)	Specific Gravity
0.0761	0.8755	1274.01	0.8793
0.1064	0.8954	1263.42	0.8954
0.2569	0.9286	1252.74	0.9254
0.3659	0.9458	1240.65	0.9478
0.4161	0.9706	1225.07	0.9748
0.5168	0.9856	1211.57	0.9887
0.6589	0.9956	1201.68	0.9978
0.7546	1.0025	1192.54	1.1002
0.8456	1.1055	1184.69	1.1085
0.9058	1.1818	1176.48	1.1870

Table 3. Molar excess volume, V_m^E , isentropic compressibility, K_s^E , intermolecular free length, L_f , and relative association, R_a , between binary liquid mixtures of 1,2- dichloroethane + p-xylene.

Mole Fraction (X_1)	Molar Excess Volume, V_m^E	Isentropic compressibility $K_s, \times 10^{-7} \text{ (m}^2/\text{N)}$	Intermolecular free length, L_f (10^{-11} m)	Relative association, R_a
0.0761	-0.941	7.04	51.0155	0.0071
0.1064	-1.914	7.11	50.8688	0.0122
0.2569	-2.745	6.86	50.3771	0.0237
0.3659	-3.931	6.87	50.4029	0.0370
0.4161	-5.675	6.86	50.3889	0.0547
0.5168	-7.331	6.91	50.5604	0.1632
0.6589	-7.170	6.96	50.7198	0.3738
0.7546	-5.668	7.01	50.9326	0.7837
0.8456	-3.722	6.45	48.8236	0.9424
0.9058	-1.176	6.11	47.5496	1.0017

Table 4. Theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's (NOM) and Van Dael and Vangeel's (VD) ideal mixing relation and percentage error for 1,2-dichloroethane (1) + p-xylene (2) at 303.15 K.

x_1	$u \text{ (m s}^{-1}\text{)}$					% error			
	Experi mental	FLT	CFT	NOM	VD	FLT	CFT	NOM	VD
0.0761	1274.01	1273.45	1272.34	1275.49	1276.34	0.0439	0.1310	0.1161	0.1828
0.1064	1263.42	1261.90	1261.39	1264.34	1265.89	0.1203	0.1606	0.0728	0.1955
0.2569	1252.74	1251.89	1250.49	1253.98	1259.39	0.0678	0.1796	0.0989	0.5308
0.3659	1240.65	1239.89	1239.10	1241.58	1247.24	0.0612	0.1249	0.0749	0.5311
0.4161	1225.07	1223.89	1224.38	1226.37	1227.35	0.0963	0.0563	0.1061	0.1861
0.5168	1211.57	1209.58	1210.34	1213.48	1213.58	0.1642	0.1015	0.1576	0.1659
0.6589	1201.68	1199.43	1200.89	1203.12	1204.34	0.1872	0.0657	0.1198	0.2213
0.7546	1192.54	1190.43	1190.45	1193.78	1194.54	0.1769	0.1752	0.1039	0.1677
0.8456	1184.69	1182.95	1182.45	1185.34	1186.98	0.1468	0.1890	0.0548	0.1933

Table 5. Values of Parameters A_j of the Redlich-Kister equation and corresponding standard deviations, $\sigma(k_s^E)$ for the binary systems at 308.15K.

A_0	A_1	A_2	A_3	$\sigma(k_s^E) (T \text{ Pa}^{-1})$
1,2- dichloroethane (1) + p-xylene (2)				
91.3	-27.10	11.50	-21.40	0.12

Table 6. Intermolecular Free Length (L_f), calculated from FLT, CFT and TAP theories for binary mixtures at 308.15 K.

x_1	$L_f(FLT)/nm$	$L_f(CFT)/nm$	$L_f(TAP)$
1,2-dichloroethane (1) + p-xylene (2)			
0.1487	50.367	50.553	50.912
0.1809	50.210	50.616	50.725
0.1983	50.104	50.724	50.579
0.2328	50.015	50.887	50.316
0.3414	49.904	50.946	50.142
0.4813	49.615	51.014	49.647
0.5646	49.502	51.153	49.005
0.6479	49.254	51.203	48.702
0.7378	48.562	51.473	48.216
0.8589	47.848	51.564	48.047
0.9236	47.657	51.616	47.337

Table 7. Available Volume, V_a , calculated from FLT, CFT and TAP for binary mixture at 308.15 K.

x_1	$V_a \cdot 10^6(FLT)/(m^3 \cdot mol^{-1})$	$V_a \cdot 10^6(CFT)/(m^3 \cdot mol^{-1})$	$V_a \cdot 10^6(TAP)/(m^3 \cdot mol^{-1})$
1,2-dichloroethane (1) + p-xylene (2)			
0.1362	32.6434	31.4804	24.8689
0.1576	32.1765	31.3417	24.3420
0.2686	31.8754	30.7731	24.7814
0.3256	31.2721	30.2708	24.3844
0.3757	30.6376	29.7544	28.6804
0.4521	30.2455	29.2621	28.5585
0.5634	29.6341	28.8040	27.8134
0.6655	29.4231	28.3310	27.4710
0.7546	28.7423	27.8463	26.6126
0.8439	28.2745	27.2321	26.5734
0.9343	27.7316	26.6379	25.4214

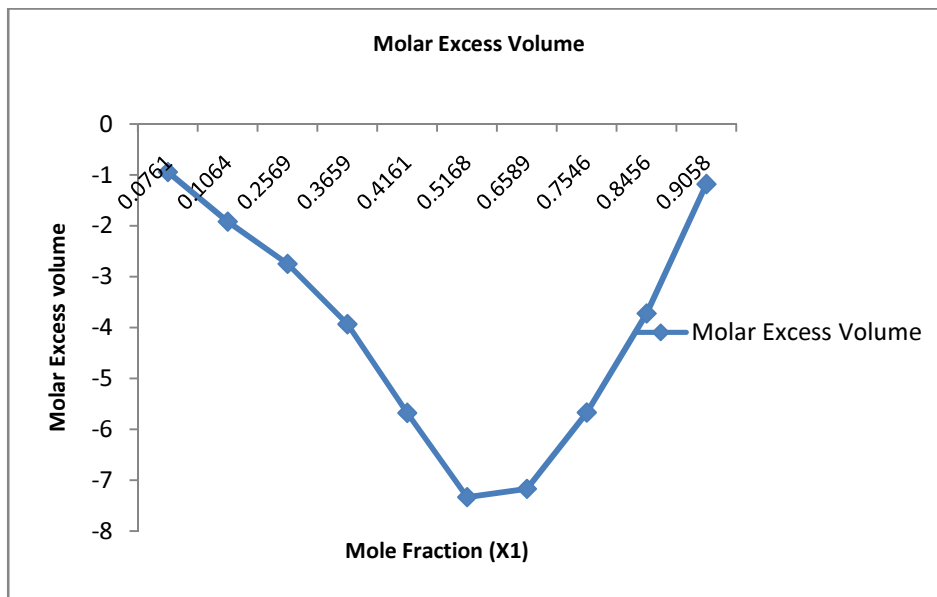


Figure 1. Variation of molar excess volume, V_m^E for the binary liquid mixture of p-xylene and 1,2-dichloroethane.

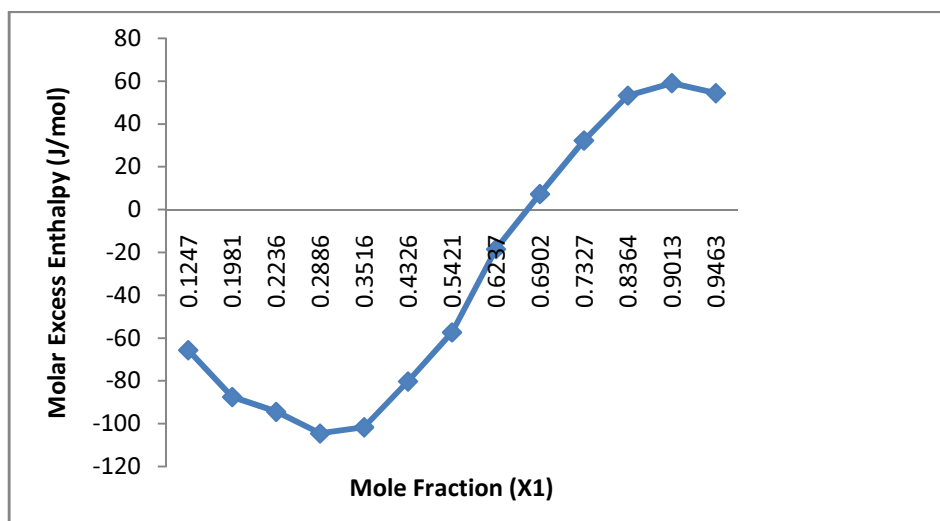


Figure 2. Variation of molar excess enthalpy (H_m^E) with the mole fraction (X_1) of 1,2-dichloroethane in p-xylene binary liquid mixture.

CONCLUSIONS

Density (ρ), ultrasonic velocity (u), molar excess enthalpy, H_m^E , and excess molar volume, V_m^E of binary liquid mixtures of p-xylene and 1,2-dichloroethane have been measured over the entire range of composition and at 308.15 K. From these experimental results, parameters such as isentropic compressibility, K_s^E , coefficients A_j , standard deviations $\sigma(Y^E)$, intermolecular free length, L_f and relative association, R_a have been estimated. The excess functions have been fitted to the Redlich-Kister polynomial equations. Intermolecular Free Length, L_f , and available volume, V_a , have been calculated from FLT, CFT and Thermoacoustic Approach. The observed positive values of K_s^E and negative value of excess molar volume V_m^E and first negative and then positive values of H_m^E for these mixtures imply that there are specific chemical attractive interaction between the two unlike molecules.

REFERENCES

1. Aminabhavi, T. M. and Banerjee, K., *J. Chem. Eng. Data* 43, 514-518 (1998).
2. Haijun, W., Goukang, Z. and Mingzhi, C. *J. Chem. Eng. Data* 26, 457-465 (1994).
3. Sandhu, J. S. and Singh, A. *J. Chem. Thermodyn.* 24, 81-84 (1992).
4. Lin, W. and Tsay, S. J., *J. Phys. Chem.* 74, 1037-1041 (1970).
5. Schneider, W. G., Ed. Hadri, D. Hydrogen Bonding. Pergamon Press, London, 55 (1959).
6. Grunwald, E. and Coburn, W. C. *J. Am. Chem. Soc.* 80, 1322-1325 (1958).
7. Coggeshall, N. D. and Saier, E. L. *J. Am. Chem. Soc.* 73, 5414-5418 (1951).
8. Pimentel, G. C. and Maclellan, A. L. The Hydrogen Bond, Freeman and Co, San Francisco 67, (1960).
9. Prasad, N. and Prakash, S. *Acustica* 36, 313-319 (1976).
10. Gopal, K. and Rao, N. P. *Acoustics Letters* 4, 164 (1981).
11. Franks, F., Quickenden, M. A. J., Reid, D. S. and Watson, B. *Trans Faraday Soc.* 66, 583 (1970).
12. Kaulgud, M. V. and Roa, K. S., *J. Chem. Soc. Faraday Trans I* 75, 2237-2251 (1979).
13. Srivastava, T. N., Singh, R. P. and Swaroop, B. *Ind. J. Pure Appl. Phys.* 21, 67-73 (1983).
14. Sette, D. *Ricerca Sci.* 25, 576-582 (1955).
15. Davanbakht, A., Long and J., Zana, R. *J. Phys. Chem.* 81, 2620 (1977).
16. Sharma, C. and Gupta, S. P. *Acoustics Letters* 11, 66 (1986).
17. Mehrotra, K. N. and Upadhaya, S. K. *Acoustics Letters* 11, 66 (1987).
18. Mehrotra, K. N., Gahlaut, A. S. and Sharma, M. J. *Colloid Interface Sci.* 120, 110 (1987).
19. Srivastava, V. N. P. *Acoustics Letters* 12, 72-76 (1988).
20. Mehrotra, K. N. and Gahlaut, A. S. *Colloid and Surfaces* 25, 180 (1989).
21. Kumar, A. *Colloids and Surfaces* 34, 313-319 (1989).
22. Schermuly, R., Schemehl, T., Gunther, A., Graimminger, F., Seeger, W. and Walmrath, D. *Am. J. Respir. Crit. Care. Med.* 156 (2) 445 (1997).
23. Wanger, M. H., Weithoff, Freidrich, S. W., Mollenhauer, I., Obiaden, M. and Boenick, U. *Bio. Phys. Chem.* 84 (1) 35 (2000).

24. Hickey, S., Lawrence, M. J., Hagan, S. A. and Buckin, V. *Langmuir* 22 (13) 5575 (2006).
25. Becu, L., Manneville, S. and Colin, A. *Phys. Rev. Lett.* 76 (13) 138 (2006).
26. Mehta and Kawaljet, S. K. *Phys. Rev. E. Stat. Nonlin. Soft Matter Phys.* 65 (2002).
27. Brasllev, M. and Grfeseex, F. J. *Colloid Interface Sci.* 251 (1) 78 (2002).
28. Alessandra, D., Aprano Camillo La Mesa and Persit, L. *Amm. J. Respir. Crit. Care Med.* 156, 445 (1997).
29. Weavers, L. K., Gimyang, F. P. J., Limei, A. Y., Rathman and James, F. *Benzene Environment Research* 77 (3) 259-267 (2005).
30. Furniss, B. S., Hannaford, A. J., Smith, P. W. G. and Tatchell, A. R. *Textbook of Practical Organic Chemistry, Longman*, 1989, 398 (2004).
31. Bhatia, S. C., Bhatia, R. and Dubey, G. *P. J. Mol. Liquid*, 144 (3) 163-171 (2009).
32. Nomoto, O. *J. Phys. Soc. Jpn.* 13, 1528 (1958).
33. Van Dael, W. *Thermodynamic Properties and Velocity of Sound*, Butterworth, London, *Chap.* 5 (1975).
34. Jacobson, B. *Acta Chem. Scand.* A6 1485-1498 (1952).
35. Schaaffs, W. *Acoustica* 33, 272-276 (1975).
36. Schaaffs, W. (1963) *Molekularakustic*. Springer Verlag, Berlin, *Chap.* 11-12.
37. Nutsch-Kuhnkie R. *Acoustica* 15, 383-386 (1965).
38. Pandey, J. D., Dev, R. and Chhabra, J. *Phys. Chem. Commun.* 6, 55 (2003).
39. Pandey, J. D., Dubey, G. P., Shukla, B. P. and Dubey, S. N. *Pramana J. Phys.* 37 (6) 433-439 (1991).
40. Benson, G. C. and Kiyohara, O. K. *J. Chem. Thermodyn.* 11, 1061 (1979).
41. Acree, W. E. *J. Chem. Eng. Data* 28, 215-216 (1983).
42. Redlich, O. and Kister, A. T., *Indust. Eng. Chem.* 40, 345-348 (1948).
43. Oswal, S. L. and Phalak, R. P. *J. Sol. Chem.* 22, 43-58 (1993).
44. Bondi, A. *Physical Properties of Molecules, Liquids and Gases*, Wiley Pub. Co., New York (1968).
45. Morcom, K. W. *Int. Data Ser., Sec. A* 56 (1973).
46. Inglese, A. and Kehiaian, H. V. *Int. Data Ser. Sec. A* 1 (1982).
47. Flory, P. J., Orwoll, R. A. and Vrij, A. *J. Am. Chem. Soc.* 86, 3507-3515 (1964).
48. Abe, A. and Flory, P. J. *J. Am. Chem. Soc.* 87, 1838-1846 (1965).
49. Aminabhavi, T. M. and Gopalakrishna, B. *J. Chem. Eng. Data*, 40, 856-861 (1995).
50. Aminabhavi, T. M., Banerjee, K. *J. Chem. Eng. Data* 43, 1096-1101 (1998).
51. Oswal, S. L., Prajapati, K. D. *J. Chem. Eng. Data* 43, 367-372 (1998).
52. Ohomuru, K. K. and Murakami, S. *J. Chem. Thermodynamics* 19, 171-176 (1987).
53. Venkatesu, P. and Rao, M. V. P. *Fluid Phase Equilibria* 98, 173-178 (1994).
54. Jacobson, B. *Acta Chim Scand* 6, 1485-1497 (1952).
55. Internet, as per data provided in advanced chemistry development Inc, Adelaide Street, West Toronto-Ontario, Canada.
56. J. S. Rowlinson, *Liquids and Liquid Mixtures*, Butterworth, London (1969).
57. L. A. K. Staveley, W. I. Tupman and K. R. Hart, *Trans. Faraday Soc.* 51, 323 (1955).